"Solidified" ammonia as energy storage material for fuel cell applications

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CTO

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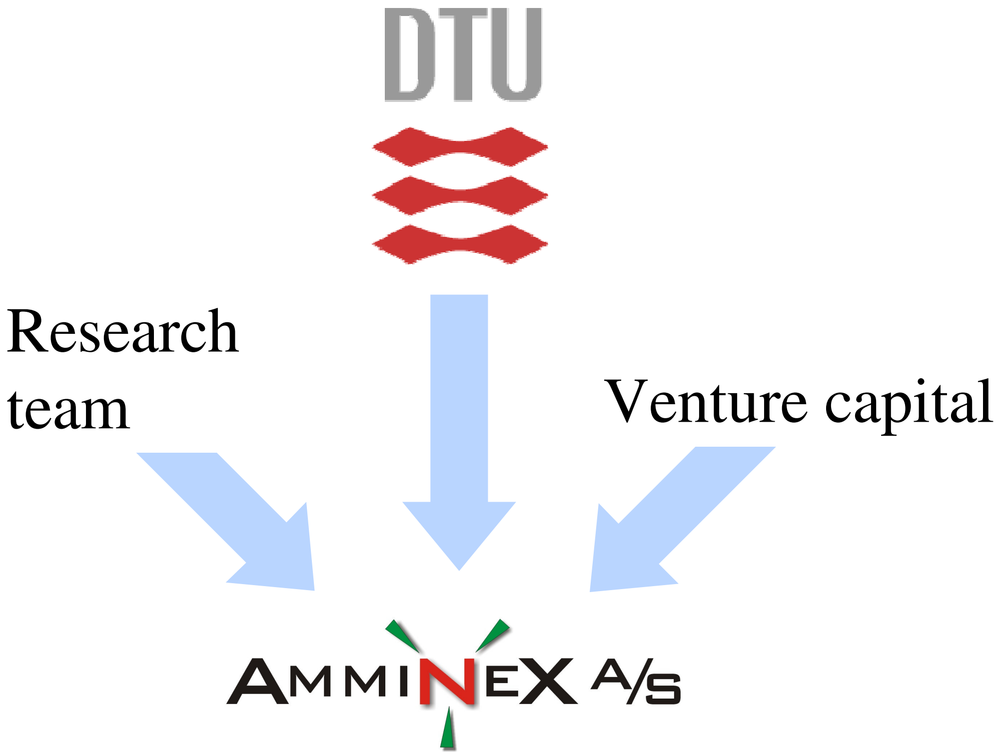
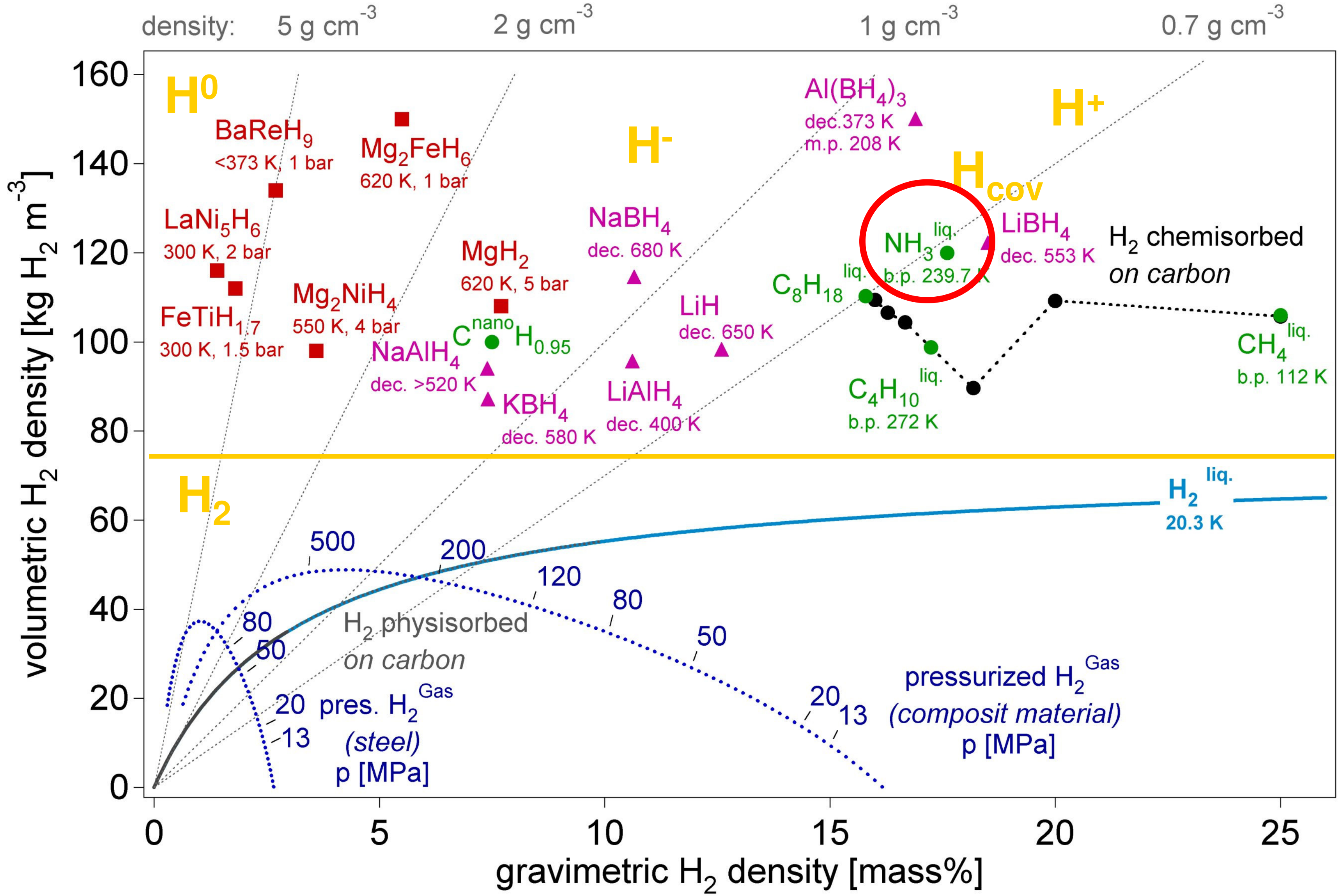
The founding of Amminex



Hydrogen storage – a challenging task

- Liquefied H_2
  - Boil-off, cost of liquefying, safety
- High pressure H_2
  - Cost of compression, safety, volumetric density
- Metal hydrides, e.g. MgH_2
  - Low bulk density, kinetics
- Complex hydrides, e.g. $NaAlH_4$, $LiAlH_4$
  - kinetics/catalyst, synthesis, reversibility
- Chemical hydrides
  - Expensive materials, reversibility, complex system
- Physisorption in porous materials
  - Material developments, synthesis, gravimetric and volumetric density

Hydrogen storage materials



A. Züttel, “Materials for hydrogen storage”, Materials Today, Septemper (2003), pp. 18-27

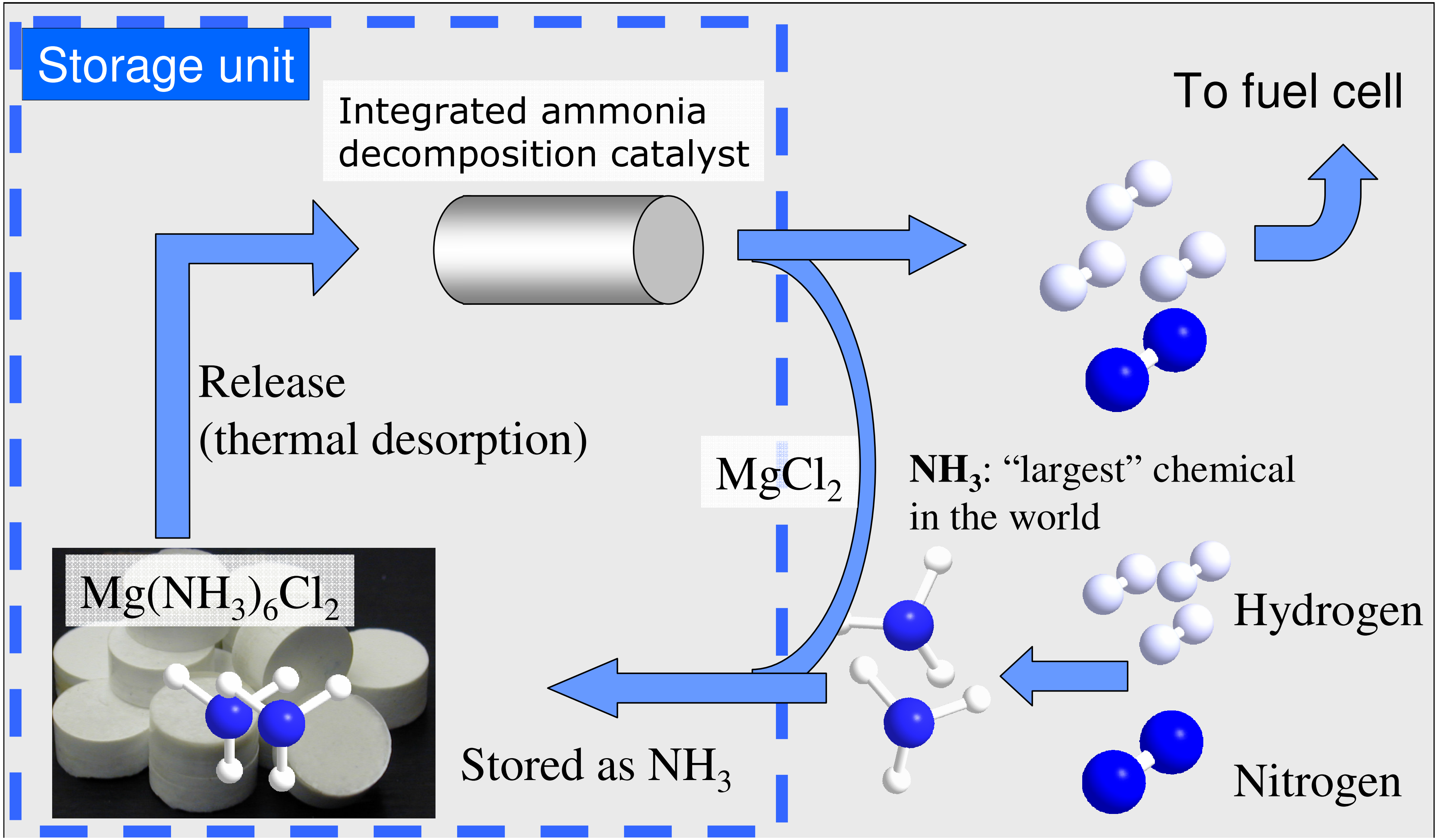
Why not ammonia?

- Dense liquid; ~ 18% of hydrogen
- Optimized catalyst exist
- Easy to reform to H_2

- But liq. NH_3 is normally considered too dangerous

!!??

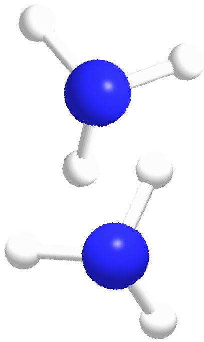
The ammonia-based competitor to metal hydrides: *metal ammine complexes*

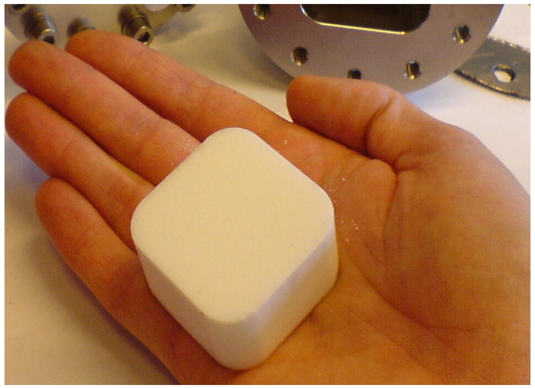


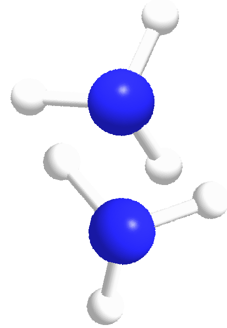
Dense and safe ammonia storage:

Controlled release from metal ammine complexes

<u>The ammonia content</u>	
$Mg(NH_3)_6Cl_2$:	38.1 mol NH_3/l
Liquid ammonia:	40.1 mol NH_3/l



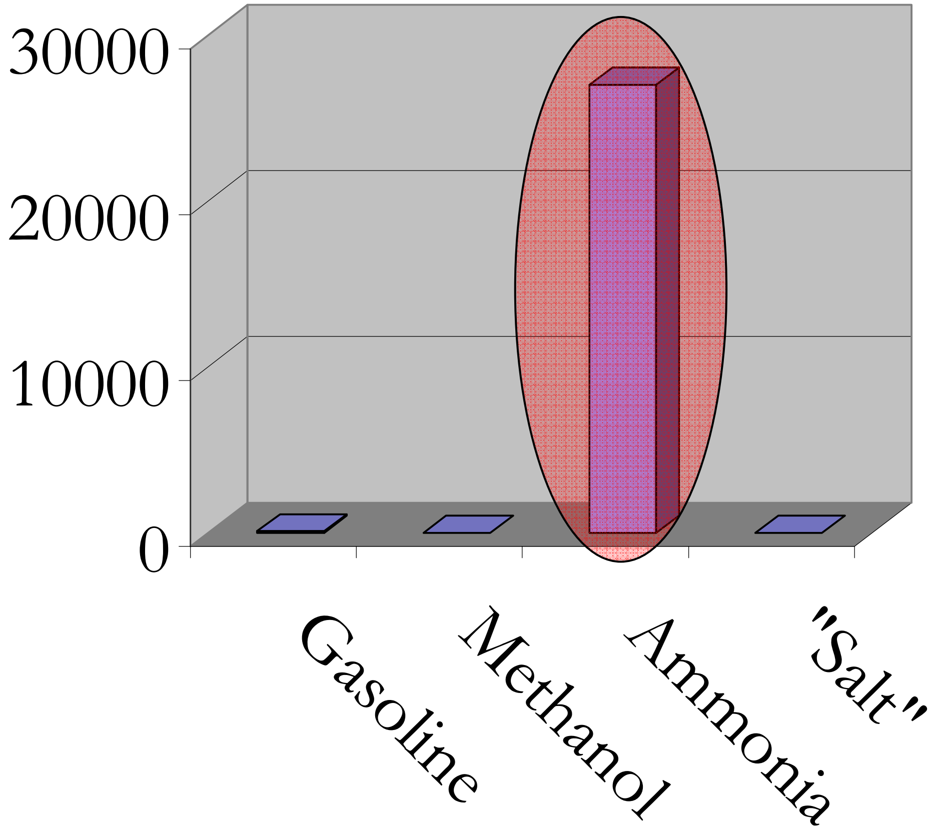




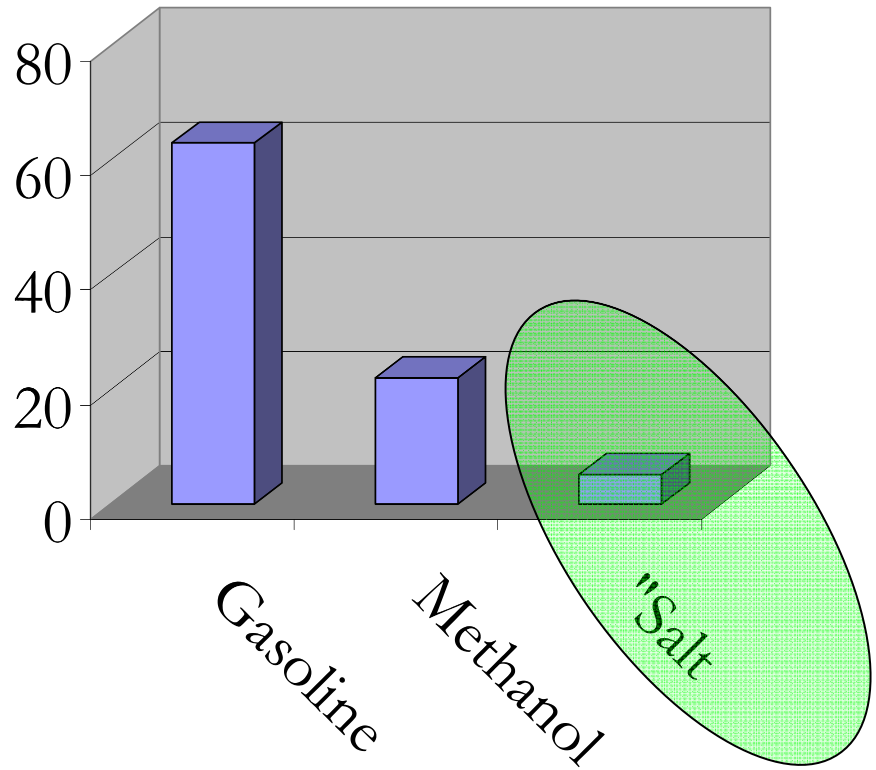
Reversible ammonia storage:

$$MgCl_2 + 6NH_3 \rightleftharpoons Mg(NH_3)_6Cl_2$$

Volatility-to-toxicity ratio*



1 liter liquid ammonia
=> 1.1 liter storage material
=> 1.3 kg storage material
=> 4000 times lower volatility



* Vapor pressure divided by IDLH (NIOSH) partial pressure

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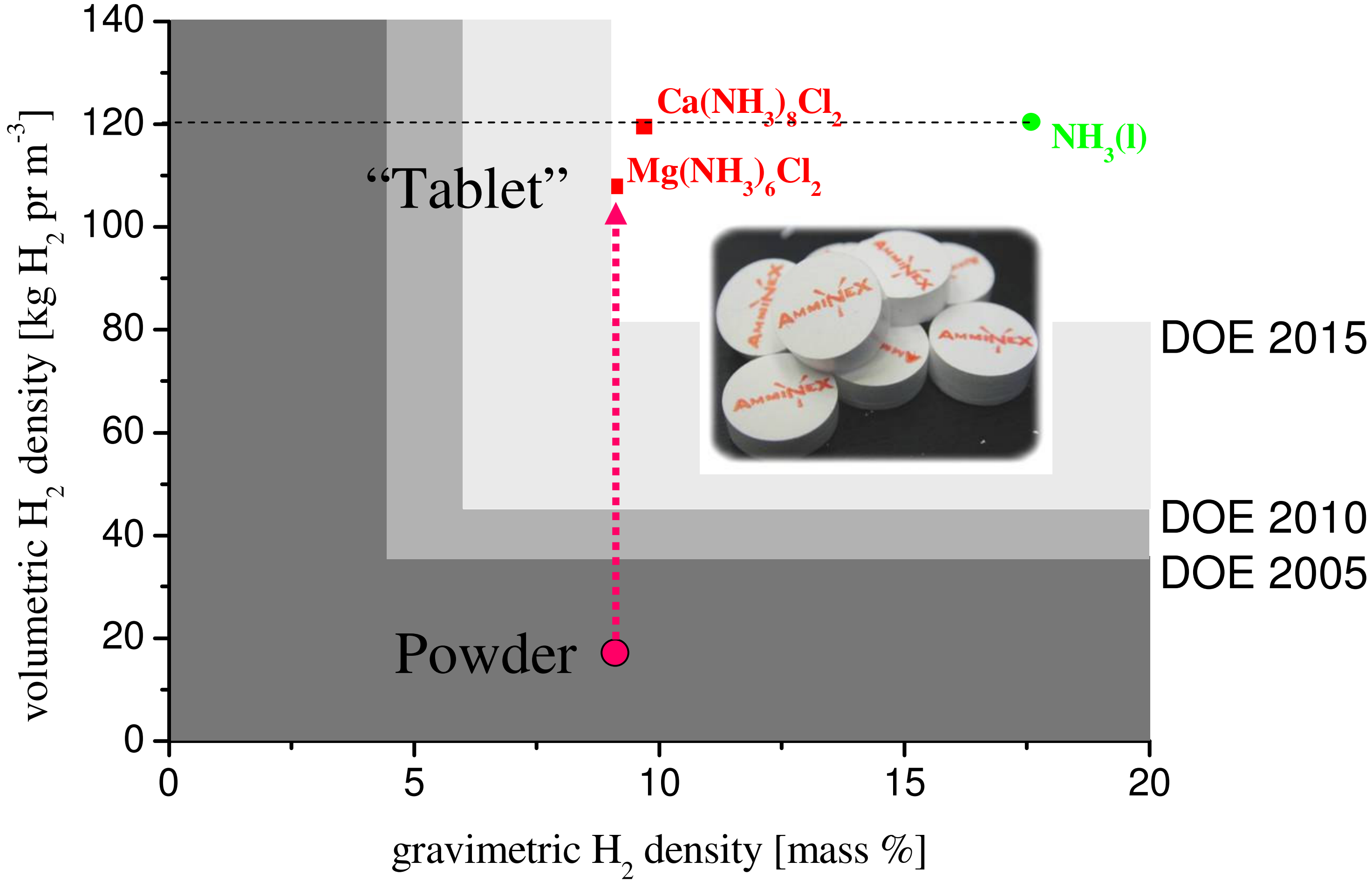
Storage capacity



*Low-pressure storage tank not included

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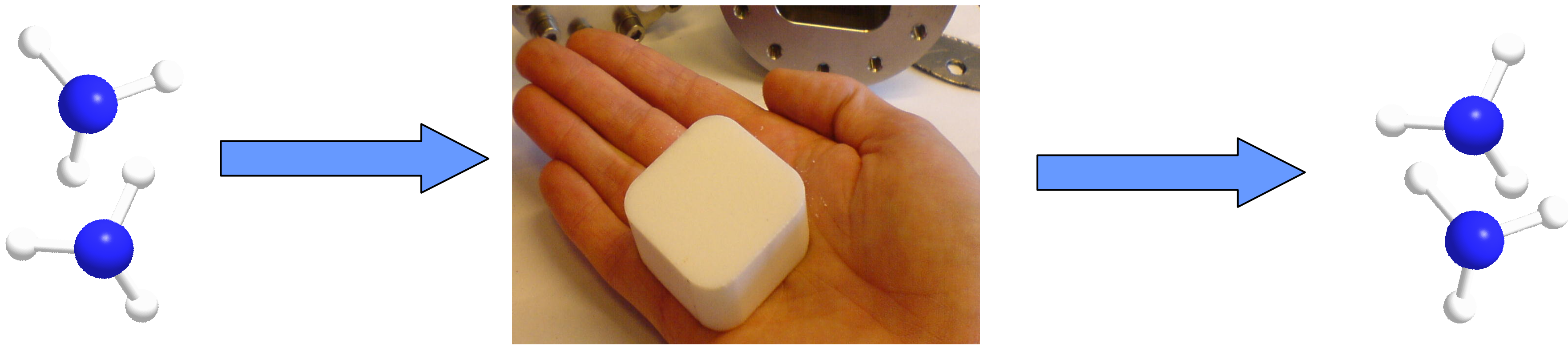
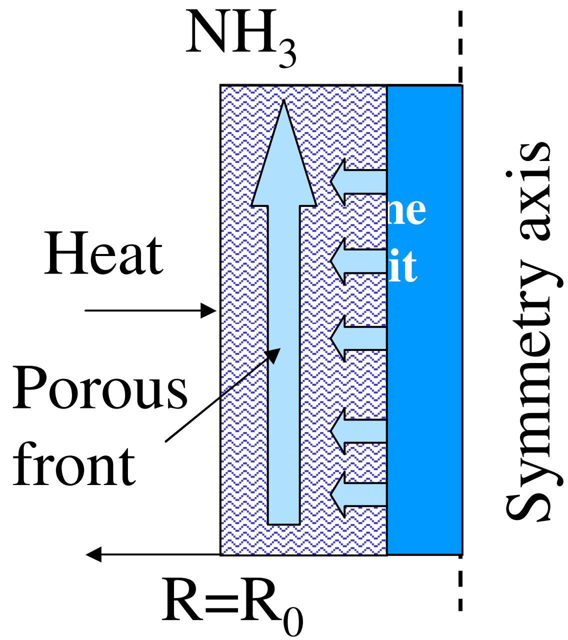
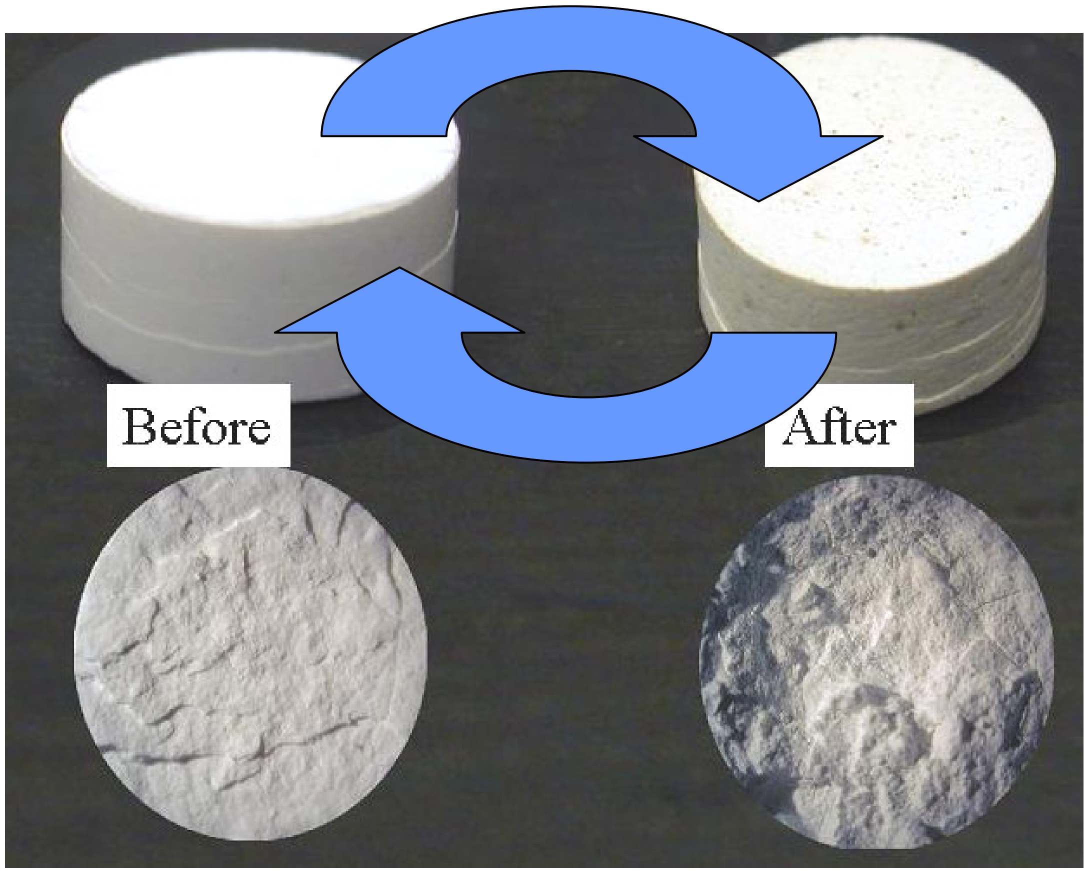
The 100 g sample

- 100g “block”
- 51.7g NH_3 stored
- 74 liter NH_3(g) at STP
- **890 bar** “NH_3” (**1330 bar** “H_2” eq.)



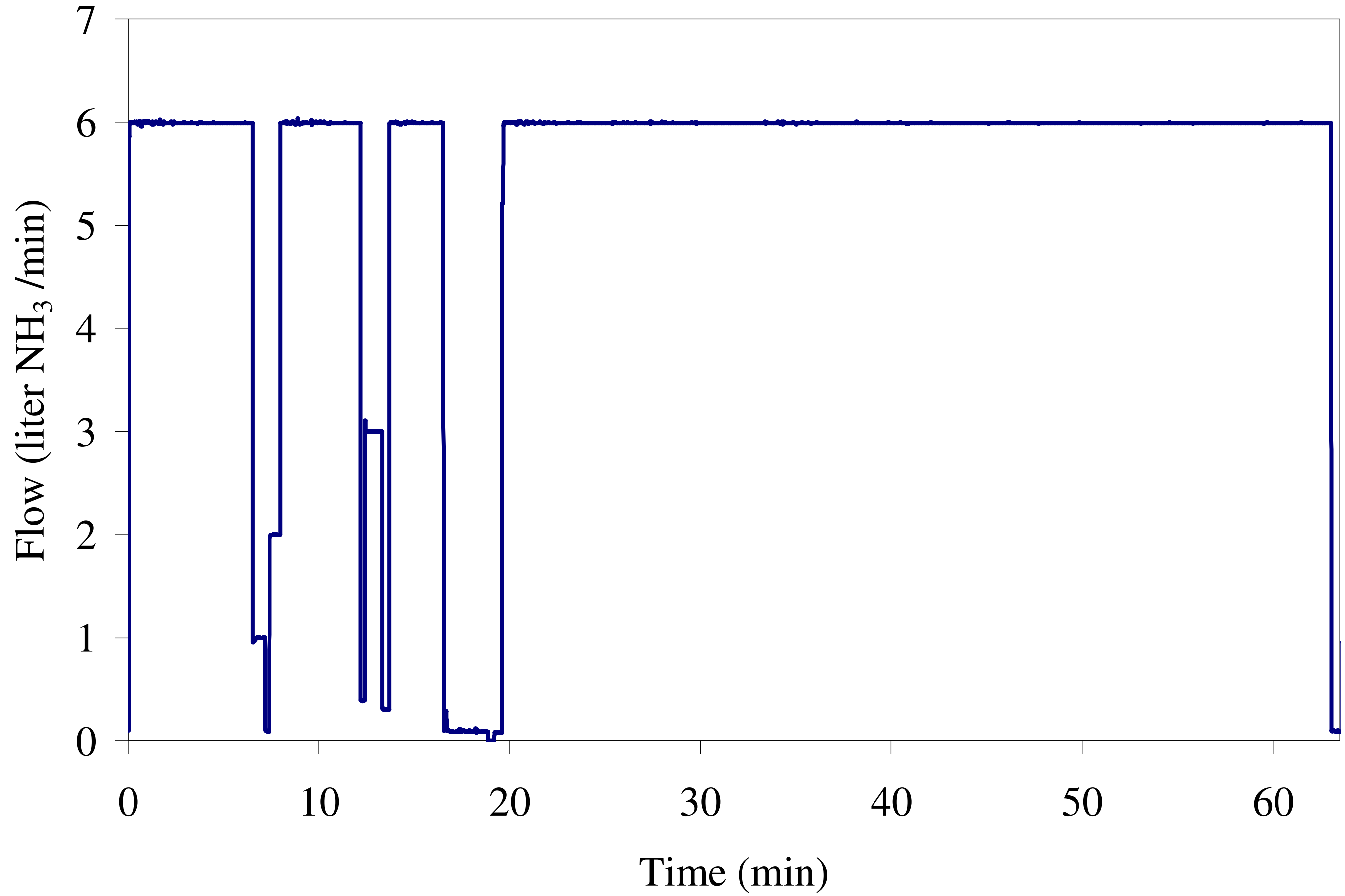
Getting NH_3/H_2 out of dense rods: a self-generated nanoporosity





High release rate demonstrated (2kg demo unit)

A stable flow of 6 liter/minute was demonstrated for several hours.
Dynamic response possible.



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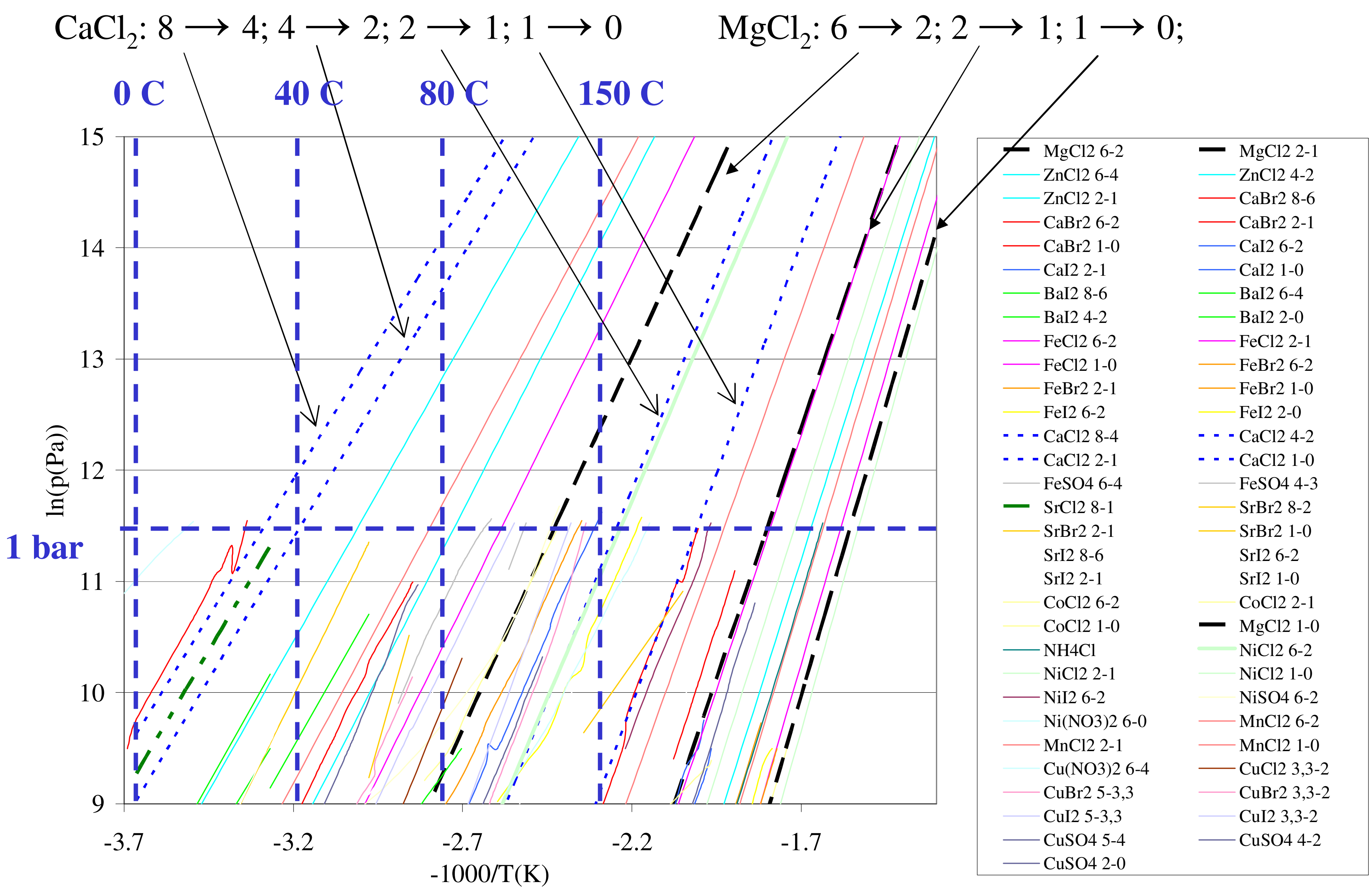
Several classes of materials

- Low "volatility" – higher operating temperature
  - High-T PEM, alkaline, SOFC
- Higher "volatility" – low operating temperature
  - Standard PEM systems



$CaCl_2$: 8 ⟶ 4; 4 ⟶ 2; 2 ⟶ 1; 1 ⟶ 0
$MgCl_2$: 6 ⟶ 2; 2 ⟶ 1; 1 ⟶ 0;
0 C
40 C
80 C
150 C
1 bar
ln(p(Pa))
-1000/T(K)
15
14
13
12
11
10
9
-3.7
-3.2
-2.7
-2.2
-1.7
MgCl2 6-2
MgCl2 2-1
ZnCl2 6-4
ZnCl2 4-2
ZnCl2 2-1
CaBr2 8-6
CaBr2 6-2
CaBr2 2-1
CaBr2 1-0
CaI2 6-2
CaI2 2-1
CaI2 1-0
BaI2 8-6
BaI2 6-4
BaI2 4-2
BaI2 2-0
FeCl2 6-2
FeCl2 2-1
FeCl2 1-0
FeBr2 6-2
FeBr2 2-1
FeBr2 1-0
FeI2 6-2
FeI2 2-0
CaCl2 8-4
CaCl2 4-2
CaCl2 2-1
CaCl2 1-0
FeSO4 6-4
FeSO4 4-3
SrCl2 8-1
SrBr2 8-2
SrBr2 2-1
SrBr2 1-0
SrI2 8-6
SrI2 6-2
SrI2 2-1
SrI2 1-0
CoCl2 6-2
CoCl2 2-1
CoCl2 1-0
MgCl2 1-0
NH4Cl
NiCl2 6-2
NiCl2 2-1
NiCl2 1-0
NiI2 6-2
NiSO4 6-2
Ni(NO3)2 6-0
MnCl2 6-2
MnCl2 2-1
MnCl2 1-0
Cu(NO3)2 6-4
CuCl2 3,3-2
CuBr2 5-3,3
CuBr2 3,3-2
CuI2 5-3,3
CuI2 3,3-2
CuSO4 5-4
CuSO4 4-2
CuSO4 2-0

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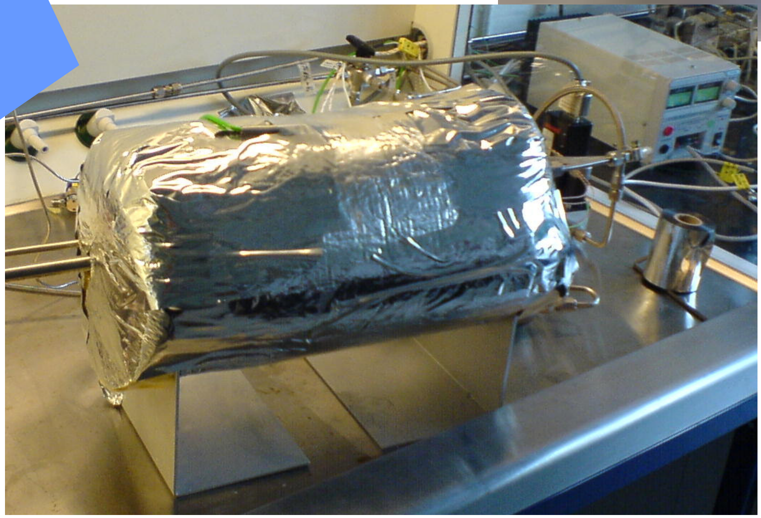
"Canisters"

- Conceptually demonstrated: 1g "tablet"
- 30g pineapple slices for H_2-generator prototype
- 100g "blocks"
- 2kg canister prototype

In-situ ammonia recharging demonstrated



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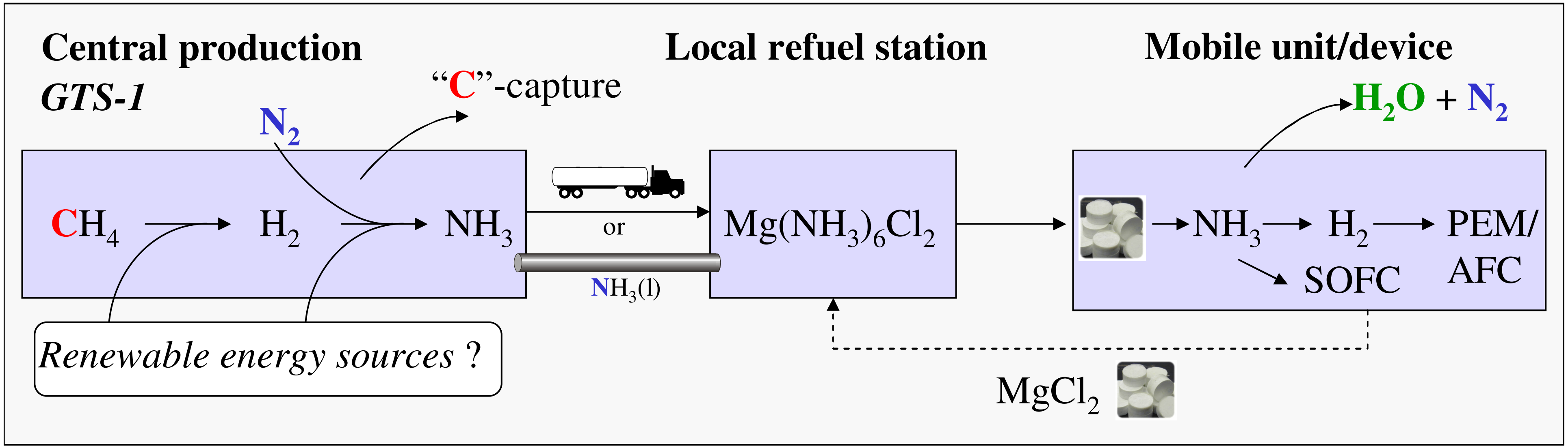
Energy density:
Comparison with normal batteries

$Mg(NH_3)_6Cl_2$
13.0 kJ/mL (theoretical)
5.2 kJ/mL (assuming **40%** energy usage)

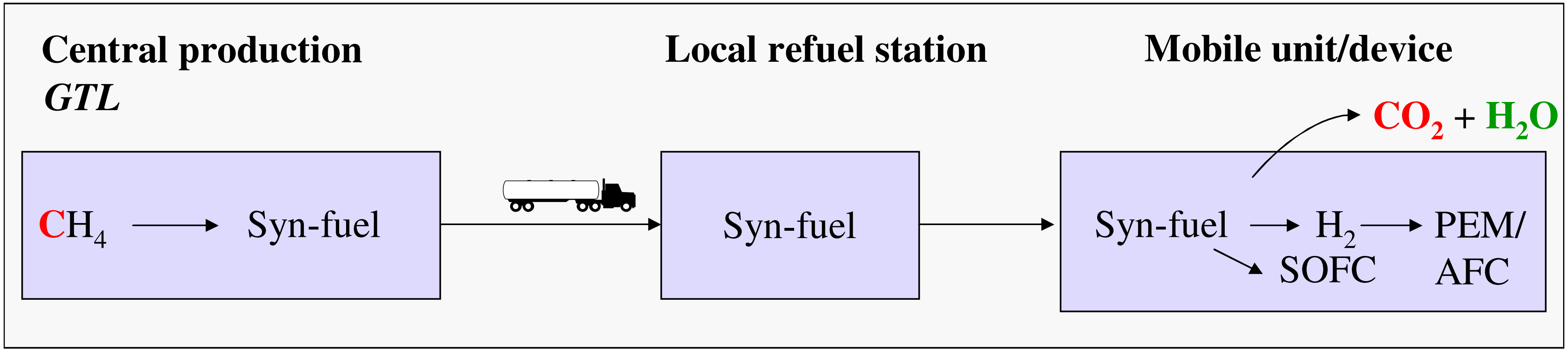
Car battery (5.5L Lead-Cd)
45 Ah, 12 V ⇒ 1944 kJ
374 mL equivalent ammine salt

0.8-1 kWh out of fuel cell ~1 liter storage unit

Possible infrastructure ?



GTL/CTL: CO_2 remains a challenge



Summary

Current status

- High demonstrated density
  - **9.1 w/w% H_2; 108 kg H_2/m^3**
- Reversible
- Fast release kinetics
- Simple to handle in open atmosphere; low pressure
- Low cost
- CO_2-free energy carrier

On-going work

- Heat management/ optimization
- PEM integration
- SOFC integration
- Packaging/re-charging

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Ammonia-enabling technology